

PROCESSIBILITY OF CORN PROTEIN BLENDS AND RESULTING PROPERTIES OF THE EXTRUDATES

Kurt A. Rosentrater¹, C. J. R. Verbeek²

¹Iowa State University, Department of Agricultural and Biosystems Engineering, Ames, Iowa, USA; karosent@iastate.edu

²University of Waikato, School of Engineering, Hamilton, New Zealand; jverbeek@waikato.ac.nz

ABSTRACT

During the last decade, the global biofuels industry has experienced exponential growth. By-products such as high protein corn gluten meal (CGM) and high fibre distillers dried grains with solubles (DDGS) have grown in parallel. CGM has been shown to be suitable as a biopolymer; the high fibre content of DDGS reduces its effectiveness, although it is considerably cheaper. In this study, the processing behaviour of CGM and DDGS blends were evaluated and resulting extrudate properties were determined. Prior to processing, urea was used as a denaturant. DDGS:CGM ratios of 0, 33, 50, 66 and 100% were processed in a single screw extruder, which solely used dissipative heating, with a 2 mm circular die. Resulting screw speeds ranged from 216 to 228 rpm, and die exit temperatures ranged from 96 to 150°C. Blends containing DDGS were less uniformly consolidated and resulted in more dissipative heating. Blends showed multiple glass transitions, which is characteristic of mechanically compatible blends. Transmission electron microscopy revealed phase separation on a micro-scale, although distinct CGM or DDGS phases could not be identified. On a macro-scale, optical microscopy suggested that CGM-rich blends were better consolidated, supported by visual observations of a more continuous extrudate formed during extrusion. As with all biological materials, the extruded blends exhibited sorption behaviour over time, the magnitude of which varied according to blend ratio. EMC values ranged from approximately 0% to nearly 50%, depending upon the humidity level and blend ratio. Nonlinear regression was successfully used to model the effects of relative humidity and blend ratio on the equilibrium moisture contents, with a coefficient of determination of 99%. Future work should aim to also characterize the mechanical properties of these blends to assess their suitability as either bioplastic feedstock or pelletized livestock feed.

INTRODUCTION

Petrochemical polymers have become ubiquitous for their excellent properties and durability. Unfortunately, they also create an enormous environmental burden. Motivations behind sustained research in reducing dependence on polymers from petrochemical sources are similar to those in energy research; a decreasing fossil fuel supply with a corresponding price increase and a widespread awareness of sustainability (Gandini, 2008).

There are two primary ways to address the energy challenge: reduce energy consumption and/or develop alternative methods of energy production. Biofuels are renewable sources of domestic energy, and are a promising alternative. One of the most frequently used materials for energy production is corn starch (Liu and Rosentrater, 2011). Ethanol production from corn can be accomplished very efficiently and at a relatively low cost. Two main techniques are used to produce ethanol: wet milling and dry grind processing. The wet milling process consists of steeping the raw corn to

moisten and soften the kernels, milling, and then separating the kernel components through various processes. The primary end products are corn starch, corn oil, and ethanol (Johnson and May, 2003). Additional end-products include corn gluten feed (CGF), corn gluten meal (CGM), corn germ meal, and condensed fermented corn extractives (Loy and Wright, 2003). Dry grinding, on the other hand, has become the primary method for ethanol production in the U.S., and uses the entire corn kernel (Bothast and Schlicher, 2005). After milling, the resulting flour is combined with water, enzymes, and additives and is then cooked and fermented. Ethanol is extracted using distillation as well as centrifugation to remove residual non-fermentable corn kernel components, water, and carbon dioxide. The non-fermentable materials are usually combined, dried and sold as ‘distillers dried grains with solubles’, or DDGS.

The potential use of agro-polymers in the plastics industry has long been recognized. Agro-polymers are extracted from either plants or animals, such as those described above. Some of the polymers in this family can be processed directly into thermoplastic materials; however, most requires chemical modification. A further benefit is that these polymers are often by-products of other agricultural activities. Common characteristics of agro-polymers are their hydrophilicity, fast degradation rate and sometimes unsatisfactory mechanical properties, particularly in wet environments (Verbeek and Bier, 2011). These polymers can be considered an innovative and sustainable approach to reduce reliance on petrochemical polymers (Chivrac, et. al, 2009). The main technological challenge is to successfully modify the properties of these materials to account for deficiencies such as brittleness, water sensitivity and low strength.

Petroleum-based materials could potentially be replaced with renewable and biodegradable materials such as polysaccharides or proteins (Verbeek and Bier, 2011). As a result, finding new uses for agricultural commodities has become an important area of research. Although bioplastics may appear to be a perfect solution to these problems, bioplastics also have some drawbacks; most importantly the perceived competition with food production. As a result, attention is shifting to second generation bioplastics manufactured from non-potential food sources. However, one of the challenges for bioplastics is to be successfully integrated into common synthetic plastic processing routes, such as extrusion and injection moulding.

In previous work it has been shown that CGM can be used to produce thermoplastic materials (Pickering et. al, 2012). CGM has a high protein content, which makes it more suitable as a thermoplastic precursor than DDGS. DDGS has a high fibre content and a low protein content compared to CGM; however, it is much cheaper. The objectives of this research were to develop corn protein-based bioplastics by replacing portions of CGM with DDGS. In addition, processibility, morphology, and thermal properties of these blends were evaluated, along with dynamic and equilibrium relationships of these extrudates with water.

MATERIALS AND METHODS

Materials

Corn gluten meal was obtained from Consumers Supply Distributing (Sioux City, IA, USA), while the DDGS was procured from VeraSun Energies (Aurora, SD, USA), after having the lipids removed by solvent extraction (Saunders & Rosentrater, 2009). Composition of each of these protein meals is provided in Tab. 1.

Tab.1: Composition of the raw protein sources used in the study

	CGM	DDGS
Dry Matter (%)	90.8	98.0
Crude Protein (% db)	67.4	34.0
Crude Lipid (% db)	2.2	2.7
Carbohydrate (% db)	28.1	58.5
Neutral detergent fiber (% db)	5.7	50.1
Starch (% db) *	15	5
Ash (% db)	2.3	4.8

Protein Modification

Prior to processing, CGM and DDGS were mixed with 10 g urea (dissolved in 50 g water) per 100 g of protein meal. Materials were thoroughly mixed for 30 min in a rotating mixer and then sealed in plastic containers and left over night to equilibrate.

Extrusion Processing

After modification, the protein sources were blended at specific ratios and were extruded using a single screw autogenous (i.e., heat was not added externally; rather all heat was generated due to friction alone) extruder (Rietz, Extructor, Bepex International LLC, Minneapolis, MN (Fig. 1a). The die plate (Fig. 1b) consisted of 6 orifices equally spaced, 2 mm diameter each, with a total opening area of 18.85 mm². The extruder had a split barrel with three sections; the front (i.e., die) section was fitted with two thermocouples, with one placed at the entry to the section (which recorded T₂) and the second placed near the die exit (which recorded T₁). A power meter (HIOKI 3196, HIOKI E.E. Corporation, Nagano, Japan) was used to continuously record power consumption.

Extrusions were carried out in duplicate for each blend combination (i.e., n = 2 for each treatment) following a completely randomized order. The input feed rate was set ensure steady state operation of the extruder, and was approximately 132 kg h⁻¹ (SD =11.3). After processing, the extrudates were cooled to room temperature, dried at 40°C for 24 h, then stored in sealed polyethylene bags at room temperature until further analysis.

Analysis

Particle size of the raw and modified blends was determined using a particle size analyser (Camsizer, Horiba Instruments, Irvine, CA, USA). Thermal conductivity and diffusivity of the raw and modified blends were determined using a thermal probe (KD2, Decagon Devices, Pullman, WA, USA). Heat flows and glass transition temperatures were determined using a differential scanning calorimeter (DSC 822e, Mettler-Toledo, Inc., Columbus, OH).

Consolidation

Consolidation was assessed based on optical images at 10x magnification. Each image was adjusted for brightness and contrast using ImageJ software. ImageJ was used for edge detection using colour images after which they were converted to binary images.

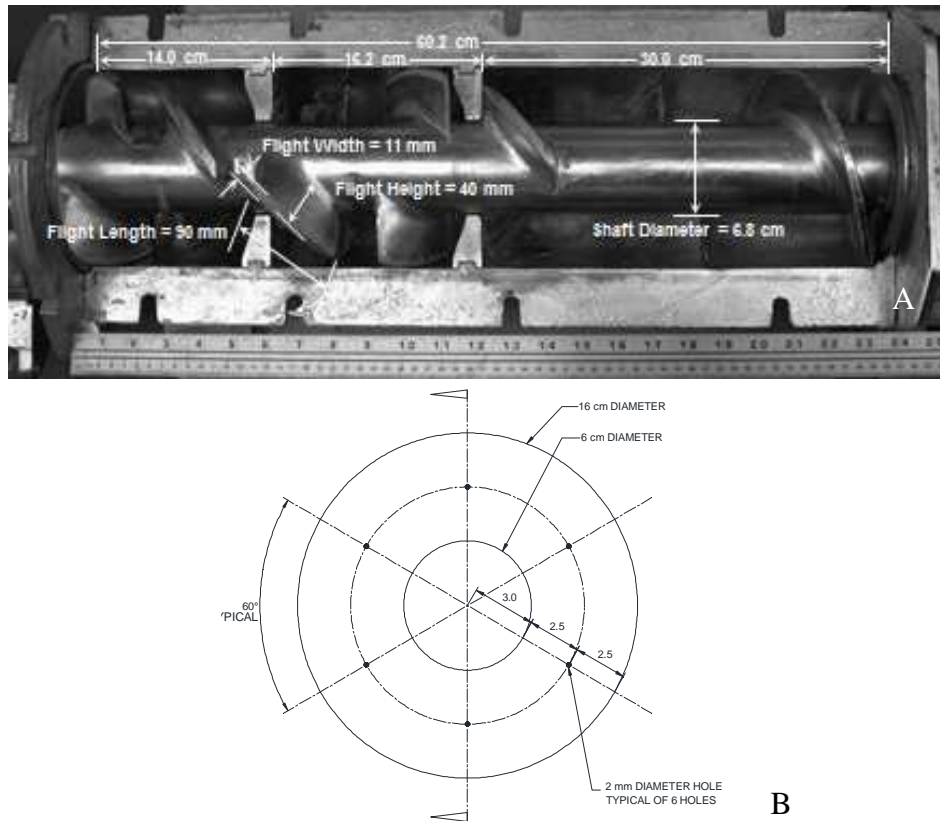


Fig. 1: A) Extruder barrel configuration; B) die plate schematic

Based on a circular section of the image the percentage black and white areas can be calculated corresponding to consolidated and non-consolidated areas.

Optical micrographs & TEM

Transmission electron microscope images were taken using a JEOL JEM2100F field emission instrument. Samples were imbedded in epoxy after osmium tetroxide and glutaraldehyde fixation. Optical images were collected using a digital microscope (Digital Blue).

Moisture Sorption

Moisture contents of all materials were determined by drying in a laboratory oven at 60°C for 24 h. Equilibrium moisture sorption for each of the extruded blends was determined by placing extrudates in sealed containers with saturated salt solutions (Tab. 2), which resulted in various relative humidity levels in each container, and then measuring sample mass over time.

Tab.2: Saturated salt solutions used to determine moisture sorption over time

Salt	Water Activity (-)	Salt	Water Activity (-)
Lithium Bromide	0.072	Sodium Bromide	0.587
Lithium Chloride	0.144	Sodium Chloride	0.756
Potassium Acetate	0.243	Ammonium Chloride	0.790
Magnesium Chloride	0.428	Lithium Acetate	0.799
Potassium Carbonate	0.439	Barium Chloride	0.932

Experimental Design

Both the DDGS and the CGM protein meals were modified by combining 100 parts protein meal, 50 parts water, and 10 parts urea 24 h prior to processing. Just before extrusion, blends were formulated (on a mass basis) to consist of DDGS:CGM ratios of 0:100, 33:66, 50:50, 66:33, and 100:0. Two replicate extrusion runs per each of the five blends were used, for a total of 10 extrusion runs.

RESULTS AND DISCUSSION

Protein Modification

As DDGS level increased, mean particle size increased, thermal conductivity decreased, and thermal diffusivity increased (Fig. 2). This was due primarily to a greater proportion of fiber replacing protein in the blends as DDGS level increased. Modifying the protein structures with urea shifted this behavior, although the trends post-modification were similar. The mean particle size of the modified protein meals did not increase as readily as when DDGS level increased, nor did the thermal conductivity decrease as rapidly. Further, post-modification the rate of thermal diffusivity increase declined as well. As fiber level (i.e., DDGS) increased in the blend, the protein level dropped, and even though the urea modified the protein which was present, the drop in protein was sufficient to reduce the impact of the fiber/protein changes vis-à-vis these physical properties.

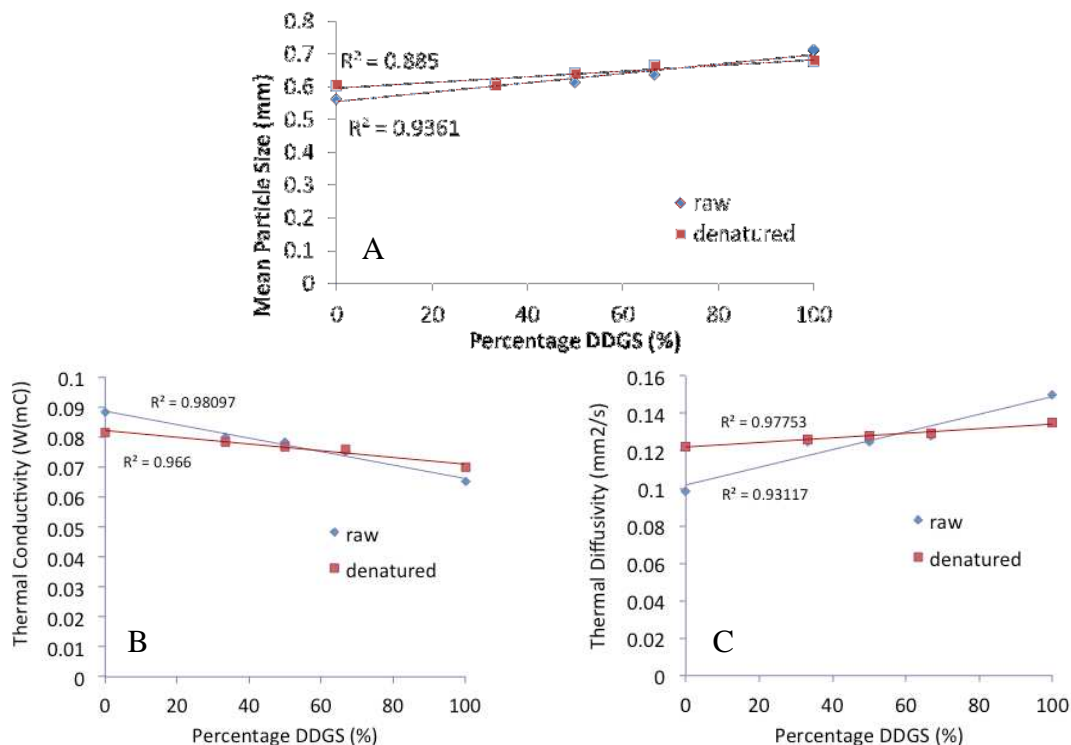


Fig. 2: Physical properties of raw and modified protein blends. A) Mean particle sizes; B) Thermal conductivity; C) Thermal diffusivity

Thermal analysis indicated that both CGM and DDGS appeared to have multiple glass transition (T_g) temperatures (Fig. 3A), which was due to these protein meals each being composed not only of corn protein, but also lipids, fibres, other carbohydrates, etc.

Modification with urea appeared to shift the glass transition points to lower temperatures (Fig. 3B).

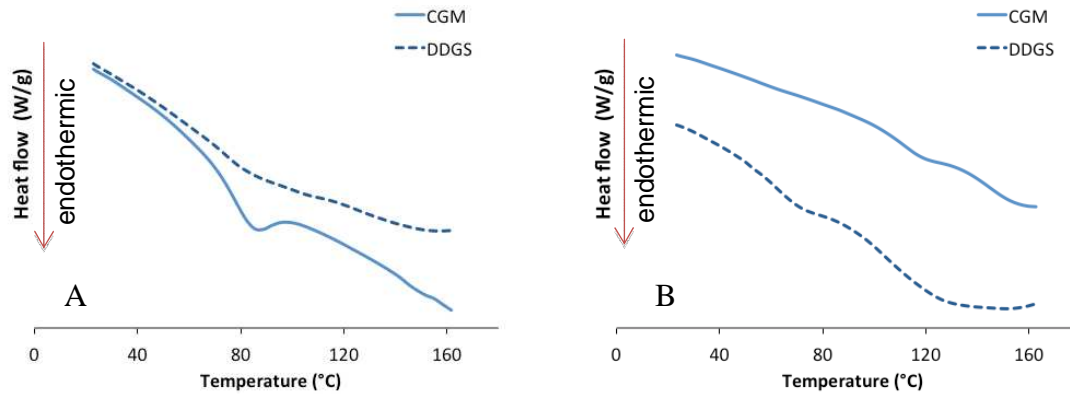


Fig. 3: Thermograms of A) raw, and B) modified protein meals

Extrusion Processing

Power consumption curves for each blend generally followed similar trends (Fig. 4A), with distinct changes after the first extruder chamber became filled, when the second chamber became filled, when the third was filled, at which point quasi-steady state was achieved, even though all blends continued to show power consumption increases over time, which were due to shear forces generating frictional heat, cooking, and then further modifying the protein structures. Integrating to find the area under each power curve provides total power consumed during each processing run. In general, as the DDGS level increased in the blend, the overall power consumption increased (Fig. 4B). This was due to the increasing levels of fibre, which is not functional compared to protein, and thus additional processing inputs were required to process the blends.

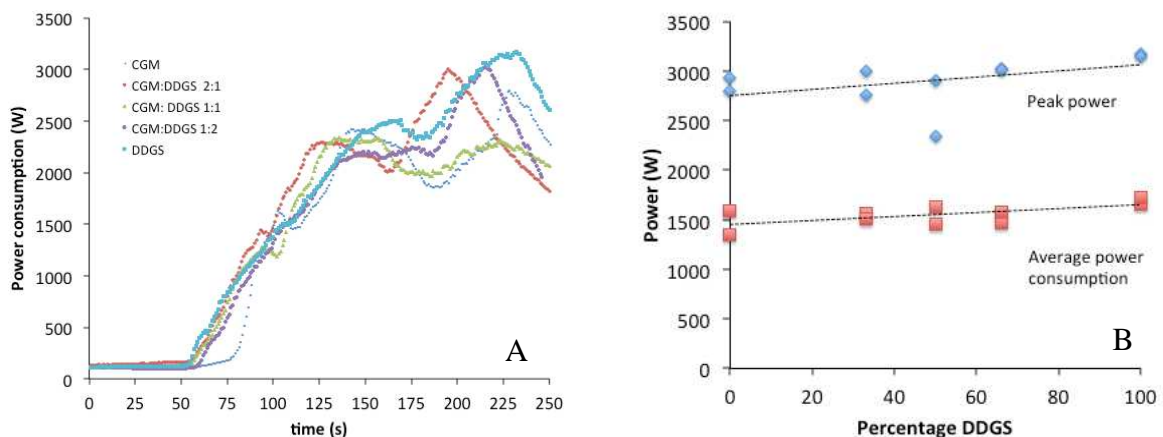


Fig. 4: Power consumption during extrusion processing; A) total power data; B) peak and average power consumption for each blend

Temperature rise in the extruder barrel (Fig. 5), both zone 1 (central extruder chamber) and zone 2 (chamber at which the material exited the die), increased over time. Zone 2 always had a much higher temperature response because that was the chamber where the majority of frictional energy was imparted to the dough; zone 1 was primarily a zone for material transfer. CGM appeared to heat more rapidly (Fig. 5A) than did DDGS (Fig.

5B). As DDGS level in the blend increased, the average temperature in the extruder (both zone 1 and zone 2) had a curvilinear response (Fig 5C), so that as DDGS level increased, processing temperatures, in general, declined.

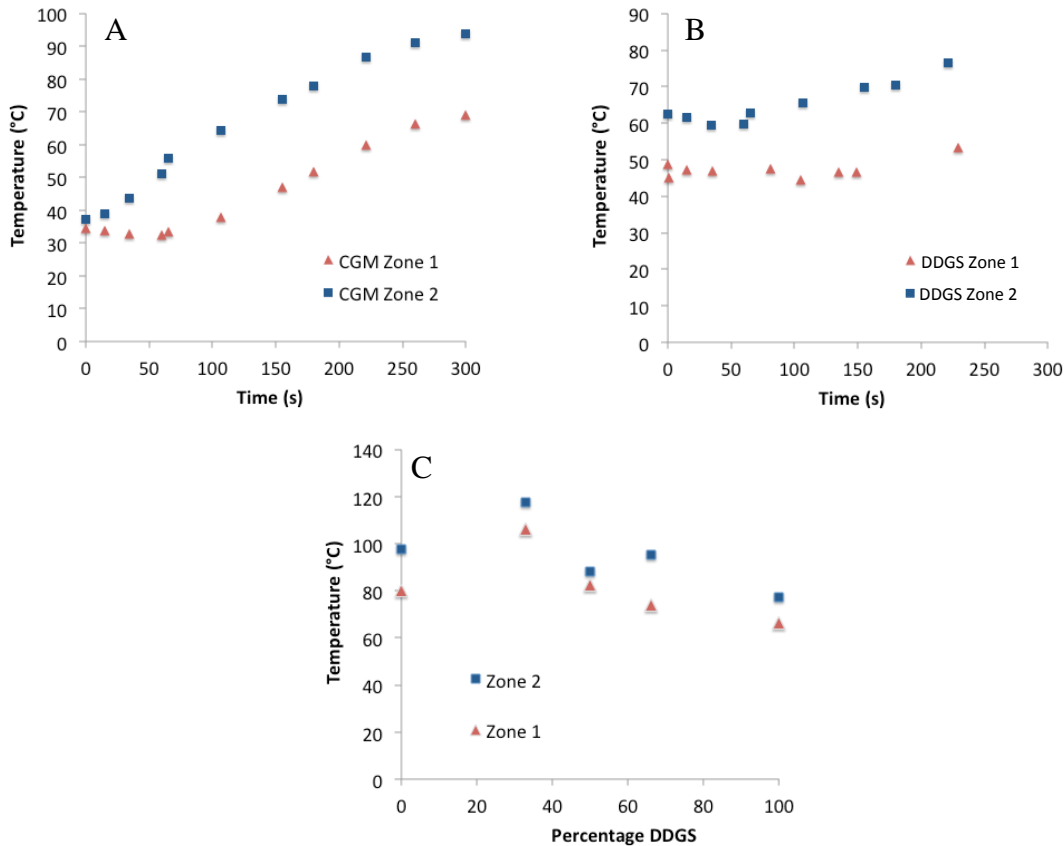


Fig. 5: Temperature behaviour in extruder Zone 1 and Zone 2 (die zone) during processing; A) modified CGM; B) modified DDGS; C) average temperatures as a function of blend ratio

Consolidation

In Fig.6 the change in consolidation as a function of blend composition is shown. Relatively poor consolidation was achieved even from pure CGM, which is slightly at odds with previous work. However, these materials were not injection moulded into test pieces, but analysed directly after extrusion. Furthermore, the extruder setup precluded high pressure build up, typically required for consolidation. Substitution DDGS for CGM reduced the consolidation from about 60 % to between 40 - 45 %. It was thought that the non-protein fraction in DDGS would be the main reason for this reduction as the fibre content will not be able to be consolidated as part of the polymer matrix. Despite this, a semi-continuous extrudate still formed, suggesting enough consolidation required for bioplastic formation.

The morphology of CGM and DDGS after extrusion was also analysed using TEM (Fig.7). It can be seen that the initial particulate structure of CGM and DDGS has been destroyed. In addition, the difference between CGM and DDGS is clearly visible. The darker, well-consolidated regions would likely represent the protein fraction, while the lighter, more strand-like features in Fig. 6B represent the fibrous fraction in DDGS. It is clear from the figure that there is a distinct separation between these two phases.

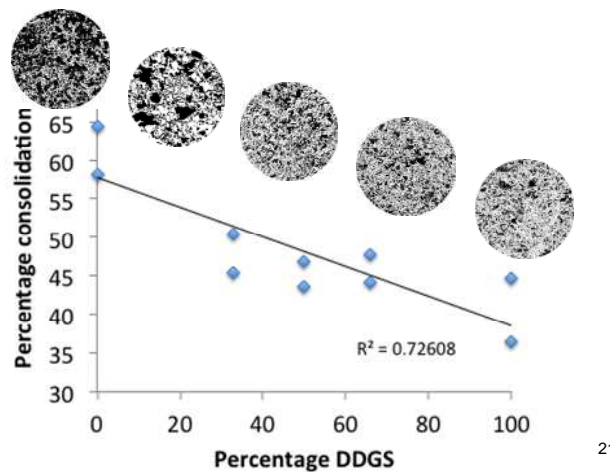
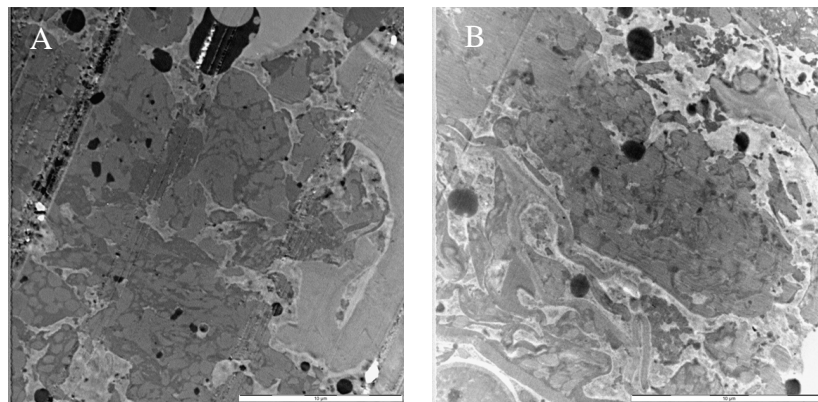


Fig. 6: Protein consolidation as influenced by blend ratio

Fig. 7: TEM images of protein meals (scale bar represents 10 μm); A) CGM; B) DDGS

Thermal Properties

The thermal properties of CGM and DDGS are complex as both these materials are in fact blends of different protein fractions as well as carbohydrates; each of these could give rise to a distinct T_g . It was seen in Fig. 3 that CGM and DDGS both showed thermal transitions thought to be associated with T_g s of different materials in each feed protein. When mixed, the thermal properties of these materials were similar, showing two T_g s (Fig. 8). The second T_g was slightly obscured in the raw blend, but became apparent after modification, which also lowered both glass transition temperatures. Both T_g s were further lowered after extrusion, suggesting some chain rearrangement and plasticization. Complete miscibility was not achieved, as two T_g s were always observed and was consistent with TEM images suggesting some degree of phase separation.

Moisture Sorption

All extruded corn protein blends exhibited sorption behaviour over time, and all achieved moisture equilibrium in less than three weeks. In terms of dynamic behaviour (Fig. 9), all blends appeared to follow that of Peleg (Ganesan et al., 2007). To achieve equilibrium moisture contents (EMC) (Fig 10), all protein blends followed non-linear behaviour which could be described by Henderson (Ganesan et al., 2008). EMC values ranged from approximately 0% to nearly 50%, the magnitude of which varied according to blend ratio and water activity (relative humidity) of the environmental chamber headspace.

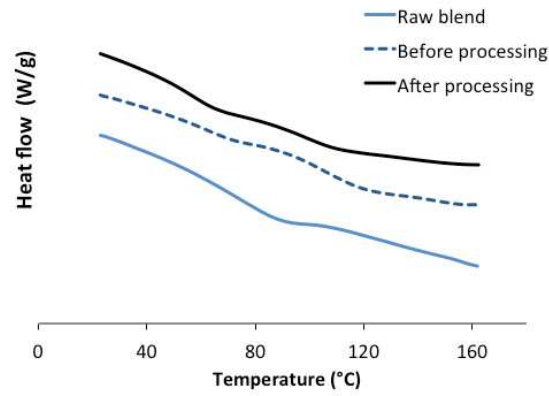


Fig. 8: Thermograms of 50% DDGS and 50% CGM blends, at different stages of processing

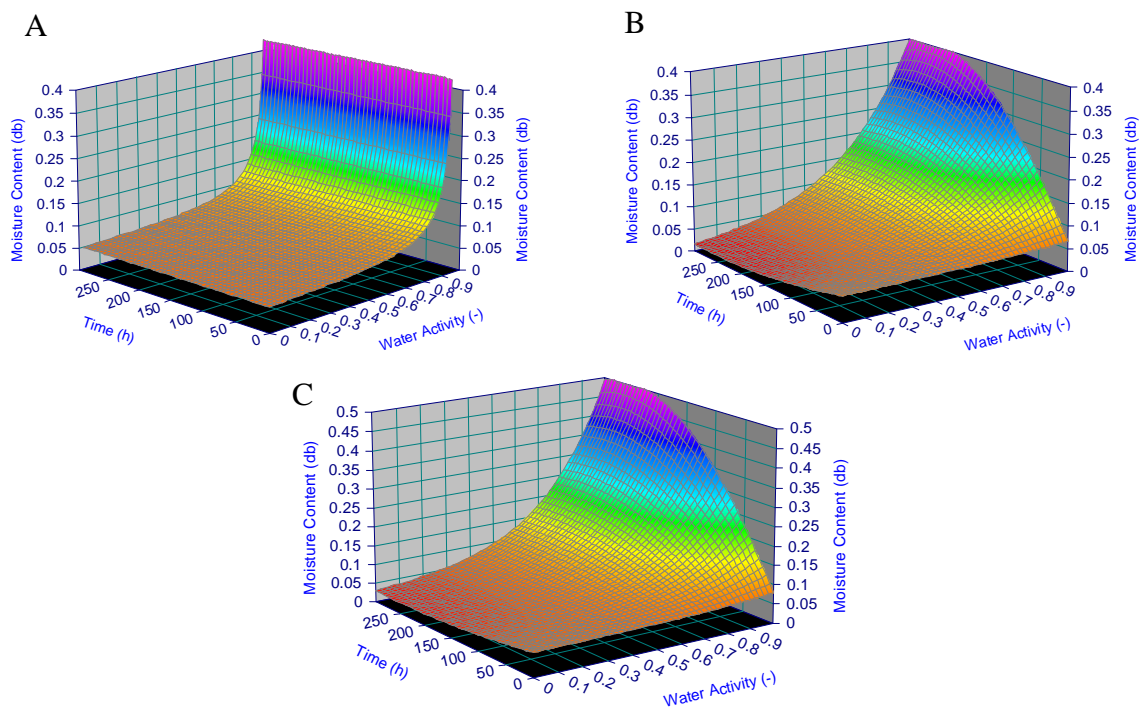


Fig. 9: Dynamic moisture sorption over time. A) 0% DDGS; B) 50% DDGS; C) 100% DDGS.

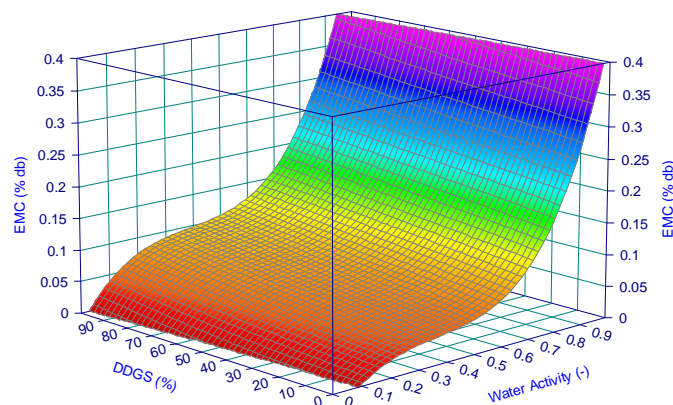


Fig. 10: Equilibrium moisture content as a function of water activity and DDGS level.

CONCLUSIONS

Extrusion processing of treated blends of DDGS and CGM resulted in modified, consolidated corn proteins. It was readily apparent that processability and resulting functionality was dependent upon the specific blend composition used, which was influenced by the protein, starch, and fibre contents of the raw materials. As the level of DDGS increased, the consolidation level decreased, as did the thermal conductivity, but thermal diffusivity and mean particle size increased. Urea treatment and extrusion processing resulted in downward shifts of the glass transition temperature compared to the raw protein meals prior to processing; as DDGS level increased, glass transition decreased as well. Dynamic and equilibrium moisture sorption was dependent upon blend, water activity, and time. Some of the differences between the CGM and DDGS blends may be due to prior processing, as the wet milling process (CGM) and dry grind (DDGS) approaches have unique processes that result in differences in protein structures. Investigating these differences is a necessary topic for further research.

REFERENCES

- Bothast, R. and M. Schlicher. 2005. Biotechnological processes for conversion of corn into ethanol. *Applied Microbiology and Biotechnology* 67(1): 19-25.
- Chivrac, F., Pollet, E.; Averous, L. 2009. Progress in nano-biocomposites based on polysaccharides and nanoclays. *Materials Science & Engineering R-Reports*. 67(1): 1-17.
- Gandini, A. 2008. Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials. *Macromolecules*. 41(24): 9491-9504.
- Ganesan, V., K. A. Rosentrater, and K. Muthukumarappan. 2007. Dynamic water adsorption characteristics of distillers dried grains with solubles (DDGS). *Cereal Chemistry* 84(6): 548-555.
- Ganesan, V., K. Muthukumarappan, and K. A. Rosentrater. 2008. Sorption isotherm characteristics of distillers dried grains with solubles (DDGS). *Transactions of the ASABE* 51(1): 169-176.
- Johnson, L. A. and May, J.B. 2003. Wet milling: the basis for corn biorefineries. Pages 449-495 in: *Corn: Chemistry and Technology*, 2nd Edition, P.J. White and L.A. Johnson, ed. American Association of Cereal Chemists: St. Paul, MN.
- Liu, K. and K. A. Rosentrater. 2011. *Distillers Grains: Production, Properties, and Utilization*. Taylor and Francis/ CRC Press: Boca Raton, FL, USA.
- Loy, D. D. and K. N. Wright. 2003. Nutritional properties and feeding value of corn and its by-products. Pages 571-604 in: *Corn: Chemistry and Technology*, 2nd Edition, P.J. White and L.A. Johnson, ed. American Association of Cereal Chemists: St. Paul, MN.
- Pickering, K., Verbeek, C.; Viljoen, C. 2012. The Effect of Aqueous Urea on the Processing, Structure and Properties of CGM. *Journal of Polymers and the Environment*. 10.1007/s10924-011-0411-4
- Saunders, J. A. and K. A. Rosentrater. 2009. Properties of solvent-extracted low-oil corn distillers dried grains with solubles. *Biomass and Bioenergy* 33: 1486-1490.
- Verbeek, C.J.R.; Bier, J.M. (2011). Synthesis and characterization of thermoplastic agropolymers., in *Handbook of Applied Biopolymer Technology*., S.K. Sharma and A. Mudhoo, Eds.; RSC Publishing; 197-242.